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Effect of a Two-Dimensional Pressure on the Curie Point of Barium Titanate

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**Effect of a Two-Dimensional Pressure
on the Curie Point of Barium Titanate**

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Massachusetts Institute of Technology
Cambridge, Massachusetts**

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EFFECT OF A TWO-DIMENSIONAL PRESSURE
ON THE CURIE POINT OF BARIUM TITANATE

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Abstract: By hydraulic means, a single crystal of barium titanate in the shape of a flat circular disk was subjected to a pressure exerted on its edges and not on its faces. A very slight pressure removed all domains that were not normal to the disk. The stress system then consisted of equal pressures on the two a axes, and no pressure on the c axis. The transition temperature increased with the square of the two-dimensional pressure, while, according to Merz, a hydrostatic pressure produces a linear drop. Using Devonshire's expansion for the free energy and the appropriate Legendre transformation, the free energy, depending on polarization and pressure, was obtained for both two-dimensional and hydrostatic stress systems. This yielded a purely linear-pressure dependence, and it was therefore necessary to supplement Devonshire's expansion with higher terms in order to obtain a quadratic effect.

While it was too difficult to evaluate the effect of pressure on the transition temperature itself when higher terms were included, it was easy to determine the effect on the Curie-Weiss temperature T_0 . This is the temperature at which the inverse susceptibility of the cubic phase extrapolates to zero, and its pressure dependence will be the subject of a future paper. For both two-dimensional and hydrostatic pressures, the

linear part of the shift of the Curie-Weiss temperature was found to depend only on the lower terms in the free energy, and provide two independent relations for determining the two g coefficients. The quadratic shift of the Curie-Weiss temperature depended on the higher terms with which Devonshire's expansion was supplemented, and a reasonable interpretation of these higher terms gave an upward direction to the quadratic shift of the Curie-Weiss temperature.

Introduction

It has long been known that substitution of strontium for barium in barium titanate ^{1, 2)} causes a drop in the Curie temperature that depends linearly on the strontium concentration. This has been explained as due to an effective decrease of the unit cell size caused by the smaller strontium ions. If, instead, the unit cell size is reduced by application of hydrostatic pressure, the transition temperature decreases with decreasing unit cell size at about the same rate. ³⁾ The substitution of lead for barium, on the other hand, raises the transition temperature at a rate depending linearly on the lead concentration. ²⁾ Lead titanate itself has a much higher Curie temperature (490°C) and is much more strongly tetragonal. ⁴⁾ In fact, optical observations on crystals grown in the laboratory ⁵⁾ show that it remains tetragonal all the way down to liquid helium temperatures, although with a rapid drop of the birefringence. The effect of hydrostatic

1) A. von Hippel and co-workers, N.D.R.C. Reports 14-300 (1944) and 14-540 (1945); A. von Hippel, Breckenridge, Chesley and Tisza, Ind. Eng. Chem. 38, 1097 (1946).

2) D. F. Rushman and M. A. Strivens, Trans. Farad. Soc. 42A, 231 (1946).

3) W. J. Merz, Phys. Rev. 78, 52 (1950).

4) G. Shirane, S. Hoshino and K. Suzuki, Phys. Rev. 80, 1105 (1950); G. Shirane and E. Sawaguchi, Phys. Rev. 81, 458 (1951).

5) H. H. Rogers, Tech. Report 56, Lab. for Insulation Research, Mass. Inst. Tech., 1952.

pressure has been discussed by Slater⁶⁾ in terms of his statistical model of barium titanate. In this model, the local potential seen by the Ti ion, that is, the potential exclusive of dipole interaction, is represented by one harmonic potential well of cubic symmetry, supplemented by a small, fourth-power term to keep the spontaneous polarization finite. If the lattice size is reduced by hydrostatic compression (or strontium substitution), the oxygen ions that surround the Ti ion tetrahedrally are pressed more tightly against the Ti ion. The consequent stiffening of the local harmonic potential well requires a greater local field due to dipole interaction to displace the Ti ion a given distance.

A two-dimensional pressure, however, should have quite a different effect, for the crystal will contract along two axes but expand along the third. If the two axes undergoing compression are cubic axes, the local potential well will acquire tetragonal symmetry and will become football shaped, or possibly even dumbbell shaped. The latter would mean that the single local potential well had become a double well, which would result in an order-disorder type of transition if the barrier between the two wells were comparable to kT . The way in which a two-dimensional pressure affects the Curie transition in barium titanate will depend very critically on how the z expansion is related to the x contraction, and particularly on how the internal field is affected by these strains. One may say that the change in the local potential well produced by a two-dimensional pressure should allow the Ti ion to displace more freely in the z direction. On the other hand, an expansion of the lattice in the polarization direction and contractions across the polarization direction should reduce the local field.

Application of Two-Dimensional Pressures

Bridgman⁷⁾ has made studies of plastic flow and fracture of a number of

6) J. C. Slater, Phys. Rev. 78, 748 (1950).

7) P. W. Bridgman, "Large Plastic Flow and Fracture," McGraw-Hill, New York, 1952.

substances under two-dimensional compression. One method was to use a specially constructed steel die that could actually push on a ductile material in two directions at once, and the other method was to exert a pull in one direction on a sample subjected to hydrostatic pressure. The latter method amounts to a two-dimensional superposed on a hydrostatic compression that is less than the applied hydrostatic pressure by the strength of the pull. In the present work, we have developed a method of applying a uniform two-dimensional compression to the edges of a disk-shaped sample with pressures up to 1000 atmospheres. While this is small compared to the range of two-dimensional pressure obtainable by Bridgman's second method, our technique has the advantage of leaving the faces of the disk exposed so that one can make optical and X-ray measurements and apply electric fields.

The method relies on a rubber "O-ring", which is a circular ring of soft rubber with a circular cross section. The O-ring is placed around the disk-shaped sample as shown in Fig. 1 and the combination is clamped in a steel clamp as shown in Fig. 2. The faces of the clamp have windows to permit direct observation of the crystal. The clamp is tightened, thereby flattening the O-ring, until the separation of the faces of the clamp is only ca. 2 mils greater than the thickness of the crystal. This clearance allows free expansion of the crystal in the direction not subjected to pressure. Oil is forced into the clamp as shown in the figure by means of a hydraulic pump. The pressure of the oil pushes the O-ring against the edges of the crystal, and the O-ring prevents the oil from leaking out. The outside seal at the point S is accomplished by another O-ring. Actually, the clamp used in the present work was designed so that one face of the clamp is electrically insulated,* observation with a microscope being sufficient to determine the transition temperature. By introducing quartz

* The electrical measurements will not be reported until a future paper.

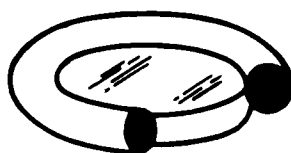


Fig. 1. Disk-shaped BaTiO₃ crystal, with rubber O-ring around it.

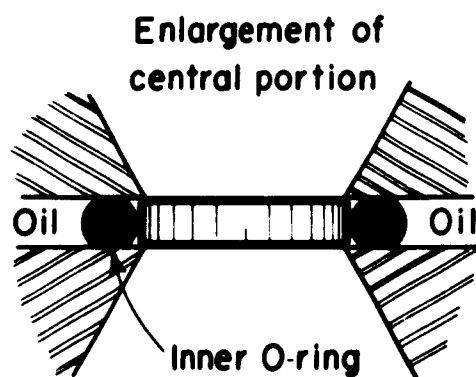
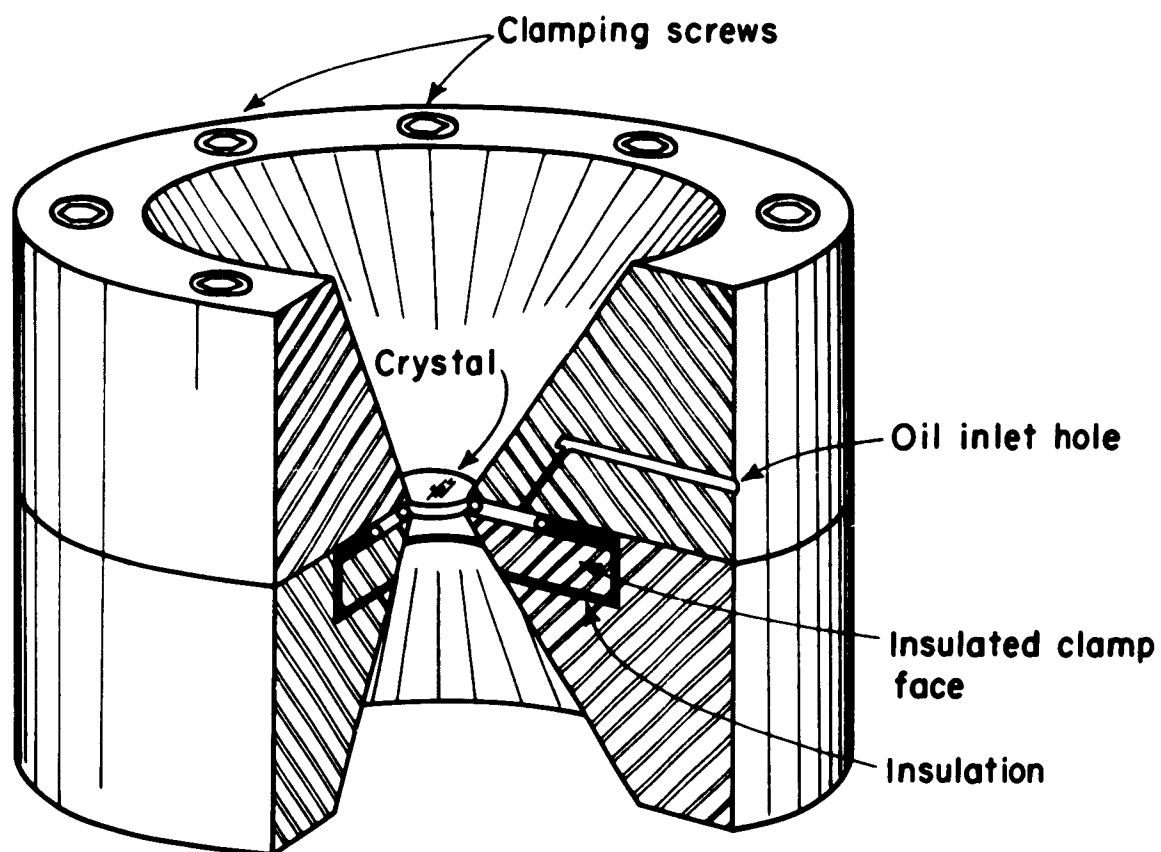


Fig. 2. Details of crystal holder for applying two-dimensional pressure.

windows, one could apply a different pressure to the faces of the crystal, which amounts to a superposition of hydrostatic pressure on a two-dimensional pressure. Since a soft rubber has a low shear modulus, sticking of the rubber to the faces of the clamp should not create a large pressure correction at the pressure used. However, if the O-ring is lubricated before clamping, the rubber can relax back and forth between the faces of the clamp fairly rapidly under changes in pressure. The data can be taken in such a manner as to allow a check on the presence or absence of a frictional correction in the pressure, which is read by means of a Bourdon gauge in the oil line.

Effect on the Transition Temperature

The disk-shaped crystal was cut from a strain-free crystal plate of cubic-growth habit and of uniform thickness. Its diameter was a little over $1/8$ in. and its thickness, ca. 20 mils. The thickness to diameter ratio of about 1 : 8 should be sufficient to prevent elastic buckling. The clamp was wound with nichrome ribbon and well insulated with glass cloth. Temperatures were measured by means of a mercury thermometer embedded deeply in the massive metal of the clamp. The transition was observed with a polarizing microscope, which revealed a considerable disturbance at the transition point. The transition was reasonably sharp at all pressures. The effect of pressure on the transition was followed by zigzagging isothermally and isobarically along the transition curve. The agreement of the downgoing transition temperatures taken isothermally and isobarically shows that the rubber transmitted the pressure without appreciable frictional correction (Fig. 3). Unfortunately, the upgoing transition could be taken only isobarically due to the insensitive needle valve in the hydraulic pump. The results show a purely quadratic dependence of the transition temperature on two-dimensional pressure. The width of thermal hysteresis increases with two-dimensional pressure. The results of Merz,³⁾ using hydrostatic pressure,

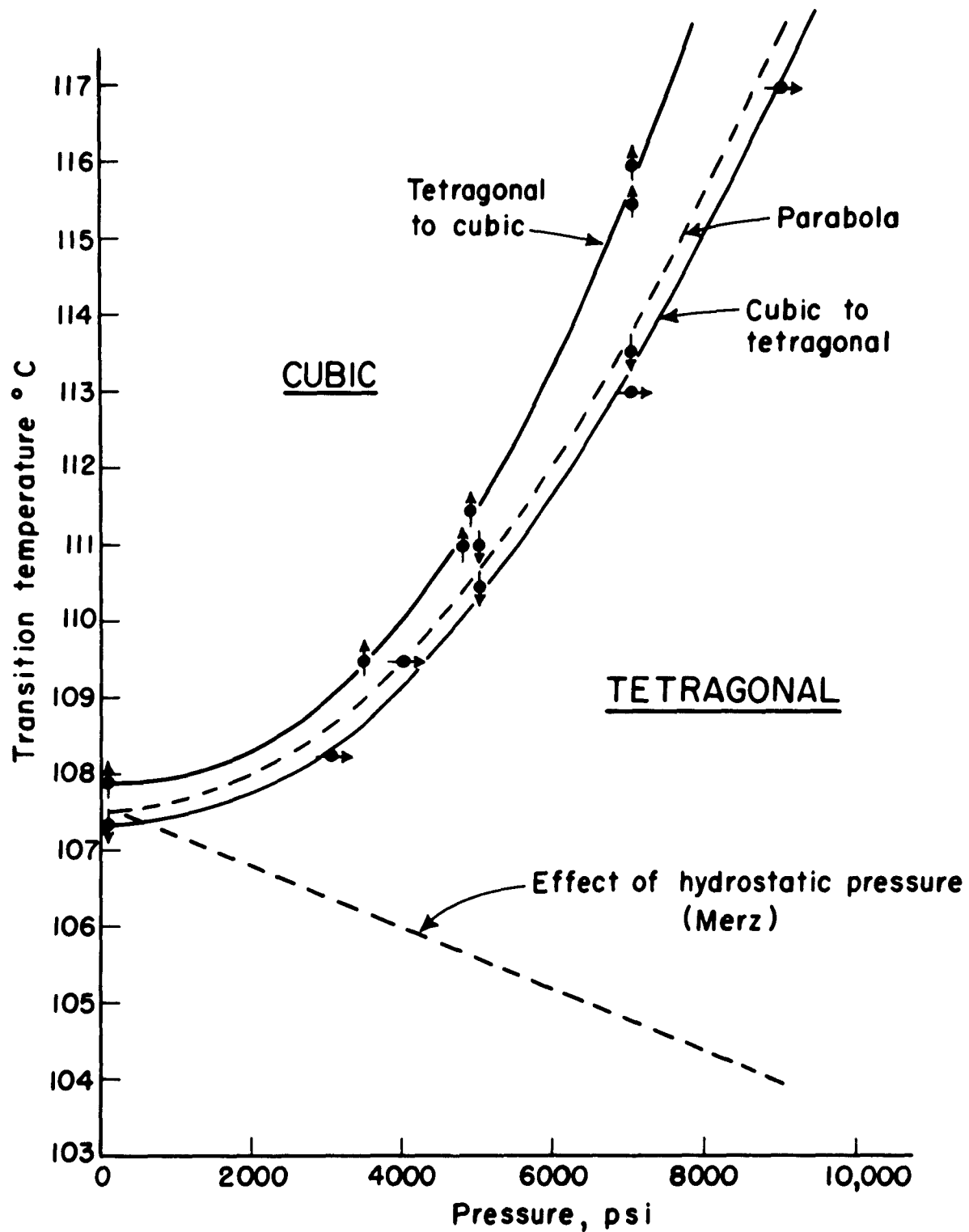


Fig. 3. Effect of two-dimensional pressure on the Curie transition in barium titanate.

show a purely linear pressure dependence. If, for convenience, the two-dimensional and hydrostatic pressure effects are symbolized by 2H and 3H, respectively, the results can be described as follows, where H is the oil pressure in atmospheres and T_c the transition temperature:

$$2H: \quad T_c = T_{c_0} + 3.1 \times 10^{-5} H^2$$

$$3H \text{ (Merz}^3\text{)}: \quad T_c = T_{c_0} - 0.0058 H$$

Effect of Pressure on Devonshire's Free-Energy Expansion

Devonshire⁸⁾ has expressed the free energy of barium titanate in terms of polarization and strain, with respect to the cubic unpolarized configuration, as

$$\begin{aligned} A_{\underline{x}, \underline{P}} = & \frac{1}{2} c_{11}^P (x_x^2 + y_y^2 + z_z^2) + c_{12}^P (y_y z_z + z_z x_x + x_x y_y) + \frac{1}{2} c_{44}^P (x_y^2 + y_z^2 + z_x^2) \\ & + \frac{1}{2} \chi'' (P_x^2 + P_y^2 + P_z^2) + \frac{1}{4} \xi_{11}'' (P_x^4 + P_y^4 + P_z^4) + \frac{1}{2} \xi_{12}'' (P_y^2 P_z^2 + P_z^2 P_x^2 + P_x^2 P_y^2) \\ & + g_{11} (x_x P_x^2 + y_y P_y^2 + z_z P_z^2) + g_{12} \left\{ x_x (P_y^2 + P_z^2) + y_y (P_z^2 + P_x^2) + z_z (P_x^2 + P_y^2) \right\} \\ & + g_{14} (y_z P_y P_z + z_x P_z P_x + x_y P_x P_y) + \frac{1}{6} \zeta'' (P_x^6 + P_y^6 + P_z^6) \end{aligned} \quad (1)$$

The underlined symbols mean the stress or strain tensors and the vector polarization, the components of all of which are in the above expression. For the present purposes, we need not consider configurations involving shears or any components of polarization aside from that in the z direction. We are thus considering the dependence of the free energy on x_x, y_y, z_z, P_z (which we shall abbreviate x, y, z, P), all other strain components (the shears) and the x and y components of polarization being kept equal to zero:

$$\begin{aligned} A_{\underline{x}, \underline{P}} = & \frac{1}{2} c_{11}^P (x^2 + y^2 + z^2) + c_{12}^P (yz + zx + xy) + \frac{1}{2} \chi'' P^2 + \frac{1}{4} \xi_{11}'' P^4 \\ & + g_{11} z P^2 + g_{12} (x + y) P^2 + \frac{1}{6} \zeta'' P^6 \end{aligned} \quad (2)$$

8) A. F. Devonshire, Phil. Mag. 40, 1040 (1949); 42, 1065 (1951).

Using the convention that a positive stress shall be a compression and a positive strain an extension, the three stress components are $X = - \partial A / \partial x$, $Y = - \partial A / \partial y$, $Z = - \partial A / \partial z$, and thus for a two-dimensional pressure

$$\begin{aligned} -H &= c_{11}x + c_{12}(y + z) + g_{12}P^2 \\ -H &= c_{11}y + c_{12}(z + x) + g_{12}P^2 \\ 0 &= c_{11}z + c_{12}(x + y) + g_{11}P^2 \end{aligned} \quad (3)$$

where the superscripts P of the elastic coefficients at constant polarization have been dropped for convenience. For a hydrostatic pressure, the stress equations (3) are the same except that the zero in the third line is replaced by a $-H$.

To discuss the Curie point and the properties associated with the z direction, we need only compare cubic and tetragonal configurations, so that the strains x and y are equal, and the stress relations become

$$3H \begin{cases} -H = \\ -H = \end{cases} \quad 2H \begin{cases} -H = (c_{11} + c_{12})x + c_{12}z + g_{12}P^2 \\ 0 = 2c_{12}x + c_{11}z + g_{11}P^2 \end{cases} \quad (4)$$

which can be solved for x and z , giving

$$\begin{aligned} 2H : \quad x &= - \frac{c_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} H - \frac{c_{11}g_{12} - c_{12}g_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} P^2 \\ z &= \frac{2c_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} H + \frac{2c_{12}g_{12} - (c_{11} + c_{12})g_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} P^2 \\ 3H : \quad x &= - \frac{(c_{11} - c_{12})}{(c_{11} - c_{12})(c_{11} + 2c_{12})} H - \frac{c_{11}g_{12} - c_{12}g_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} P^2 \\ z &= - \frac{(c_{11} - c_{12})}{(c_{11} - c_{12})(c_{11} + 2c_{12})} H + \frac{2c_{12}g_{12} - (c_{11} + c_{12})g_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} P^2 \end{aligned} \quad (5)$$

If we now substitute these expressions for the strains into the free energy (Eq. 2), remembering that $x = y$, we obtain for both cases

$$A_{x, P} = \text{terms in } H^2 + \text{terms in } HP^2 + \text{terms in } P^2 + \text{terms in } P^4 + \text{terms in } P^6. \quad (6)$$

We can now determine the free energy $A_{\underline{X}, \underline{P}}$ expressed in terms of stress and polarization, and see how it compares with the free energy as a function of polarization at zero stress,⁸⁾ for which the most recent coefficients have been given by Merz.⁹⁾ The free energy in terms of stress and polarization is related to that in terms of strain and polarization by the usual Legendre transformation:

$$A_{\underline{X}, \underline{P}} = A_{\underline{x}, \underline{P}} + \underline{x} \underline{X} \quad , \quad (7)$$

where $\underline{x} \underline{X}$ is a scalar product, and is the transformation term that must be added to Eq. (6) to obtain the free energy expressed in terms of polarization and pressure.

The transformation term is

$$\begin{aligned} \underline{x} \underline{X}_{2H} &= 2Hx = \text{a term in } H^2 - 2 \frac{c_{11}g_{12} - c_{12}g_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} HP^2 \\ \underline{x} \underline{X}_{3H} &= 2Hx + Hz = \text{a term in } H^2 - 2 \frac{c_{11}g_{12} - c_{12}g_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} HP^2 \\ &\quad + \frac{2c_{12}g_{12} - (c_{11} + c_{12})g_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} HP^2 \end{aligned} \quad (8)$$

$$\therefore A_{\underline{X}, \underline{P}} = \text{tms in } H^2 + \text{tms in } HP^2 + A_P \quad , \quad (9)$$

where A_P is the free energy as a function of polarization for zero stress, the coefficients of which have recently been given by Merz as

$$A_P = 3.7 \times 10^{-5} (T - T_0) P^2 - 1.7 \times 10^{-13} P^4 + 3.8 \times 10^{-23} P^6 \quad . \quad (10)$$

T_0 is the Curie-Weiss temperature and is about 11°C below the transition temperature, and the units are in electrostatic c. g. s. units.

The only terms through which the pressure can affect the dependence of the free energy on the polarization are terms containing both H and P, in this case (Eq. 9), the terms in HP^2 . If these terms add up to a positive quantity, pressure will raise the free energy of the polarized configurations faster than that of the unpolarized phase, and so lower the transition temperature; if they

9) W. J. Merz, Phys. Rev. 91, 513 (1953).

add up to a negative quantity, it is raised.

Having found the transformation terms (Eq. 8), we now need to calculate the contribution of $A_{\underline{x}, \underline{P}}$ to terms containing both H and P. The terms in $A_{\underline{x}, \underline{P}}$ that give terms in H and P (viz., HP^2) are as follows, where we have set $x = y$ since we are only interested in comparing cubic and tetragonal configurations: $(c_{11}+c_{12})x^2 + \frac{1}{2} c_{11}z^2 + 2c_{12}xz + g_{11}zP^2 + 2g_{12}xP^2$. For a two-dimensional pressure the sum of the terms in HP^2 in $A_{\underline{x}, \underline{P}}$ is

$$\left\{ (c_{11}+c_{12})^2 \left[c_{11}(c_{11}g_{12}-c_{12}g_{11}) \right] + \left(\frac{1}{2} c_{11} \right)^2 \left[2c_{12}(2c_{12}g_{12}-(c_{11}+c_{12})g_{11}) \right] \right. \\ \left. + 2c_{12} \left[-2c_{12}(c_{11}g_{12}-c_{12}g_{11}) \right] + 2c_{12} \left[-c_{11}(2c_{12}g_{12}-(c_{11}+c_{12})g_{11}) \right] \right\} \\ \times HP^2 / (c_{11}-c_{12})^2 (c_{11}+2c_{12})^2 \\ + (g_{11}^2 c_{12} - 2g_{12}c_{11}) HP^2 / (c_{11}-c_{12}) (c_{11}+2c_{12})$$

The second and fourth terms within the braces cancel, and the first and third terms, when added together and factored, become $2(c_{11}g_{12}-c_{12}g_{11})(c_{11}-c_{12})(c_{11}+2c_{12})$, which, when multiplied by the quantity outside braces, exactly cancels the last term in the whole expression, which means that for a two-dimensional pressure, $A_{\underline{x}, \underline{P}}$ contributes no terms in HP^2 . While, for a hydrostatic pressure the free energy $A_{\underline{x}, \underline{P}}$ contributes $-2c_{12}g_{11}/(c_{11}-c_{12})(c_{11}+2c_{12}) HP^2$. Therefore, when we add on the transformation terms (Eq. 8), the HP^2 term in $A_{\underline{x}, \underline{P}}$ is

$$\frac{-2g_{12}(c_{11}-c_{12}) - g_{11}(c_{11}+c_{12})}{(c_{11}-c_{12})(c_{11}+2c_{12})} HP^2 \text{ for } 3H \quad (11)$$

and

$$-2 \frac{c_{11}g_{12}-c_{12}g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})} HP^2 \text{ for } 2H.$$

The free energy in terms of polarization and pressure is then

$$2H: A_{\underline{x}, \underline{P}} = A_c + \left[3.7 \times 10^{-5} (T - T_o) - 2 \frac{c_{11}g_{12}-c_{12}g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})} H \right] P^2 \\ - 1.7 \times 10^{-13} P^4 + 3.8 \times 10^{-23} P^6 \quad (12)$$

$$3H: \quad A_{X, P} = A_c + \left[3.7 \times 10^{-5} (T - T_0) - \frac{2(c_{11} - c_{12})g_{12} + (c_{11} + c_{12})g_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} H \right] P^2 \\ - 1.7 \times 10^{-13} P^4 + 3.8 \times 10^{-23} P^6$$

From this it is seen that the dependence of free energy on polarization, for a given applied pressure, is only unaltered if there is a corresponding change in temperature ΔT

$$2H: \quad \Delta T = \frac{1}{3.7 \times 10^{-5}} \left[2 \frac{c_{11}g_{12} - c_{12}g_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \right] H \quad (13)$$

$$3H: \quad \Delta T = \frac{1}{3.7 \times 10^{-5}} \left[\frac{2(c_{11} - c_{12})g_{12} + (c_{11} + c_{12})g_{11}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \right] H$$

Since a purely linear dependence of the transition temperature on two-dimensional pressure is thus predicted, it is necessary to supplement Devonshire's expansion with higher terms in order to account for the quadratic effect. While it is too difficult to evaluate the effect of pressure on the transition temperature itself in the presence of the higher terms, it will be shown that the effect on the Curie-Weiss temperature T_0 is easy to determine. This may be determined experimentally by extrapolating to zero the inverse susceptibility of the cubic phase. Its dependence upon two-dimensional and hydrostatic pressure will be the subject of a future paper. It will be shown in the following section that the linear part of the shift in the Curie-Weiss temperature for two-dimensional and hydrostatic pressures gives two independent linear relations connecting the coefficients g_{11} and g_{12} , and the quadratic shifts give two linear relations connecting the 9 coefficients in the higher terms with which Devonshire's expansion may be supplemented.

Effect of Higher Terms in the Free Energy on the Curie-Weiss Temperature.

Due to the symmetry of the crystal, the strains with respect to the cubic phase depend on even powers of the polarization. Since there is a P^2 term in

the strain, the P^6 term in the free energy as a function of stress and polarization (given by Eq. (10) for zero stress) will be partially made up of terms not included in Devonshire's expansion Eq. (1). These are terms in strain P^4 , strain² P^2 , and strain³. For the present case of no shears and no polarization other than P_z , the free energy including these higher terms will be

$$\begin{aligned} A_{\underline{x}, \underline{P}} = & \frac{1}{2} c_{11}^P (x^2 + y^2 + z^2) + c_{12}^P (yz + zx + xy) + \frac{1}{2} \chi'' P^2 + \frac{1}{4} \xi''_{11} P^4 \\ & + g_{11} z P^2 + g_{12} (x+y) P^2 + \frac{1}{6} \xi'' P^6 + \beta_{11} z P^4 + \beta_{12} (x+y) P^4 \\ & + \gamma_{11} z^2 P^2 + \gamma_{12} (x^2 + y^2) P^2 + \gamma_{13} xy P^2 + \gamma_{14} (yz + zx) P^2 \\ & + \delta_{11} (x^3 + y^3 + z^3) + \delta_{12} xyz + \delta_{13} \left[y(z^2 + x^2) + z(x^2 + y^2) + x(y^2 + z^2) \right]. \end{aligned} \quad (14)$$

There is not enough accurate information to evaluate any of these higher terms, but it is easy to show that the terms with coefficients γ and δ give rise to a quadratic dependence of the Curie-Weiss temperature T_0 on the pressure.

The isotherms of polarization vs. electric field, that Merz⁹⁾ calculates from the free energy, are reproduced in Fig. 4, where the variables e and p are the field and the polarization, reduced to dimensionless variables for convenience, and t is proportional to $(T - T_0)$, where T_0 is the Curie-Weiss temperature. It is easy to show that the transition temperature occurs at the point $t = 0.75$ and in Fig. 5 the free energies corresponding to $t = 0$, $t = 0.75$ and $t = 1$ are shown schematically. The Curie-Weiss temperature $t = 0$, is clearly the temperature to which the cubic phase could be supercooled in the absence of thermal fluctuations, and the tetragonal phase could be overheated to $t = 1$ in the absence of thermal fluctuations. The Curie-Weiss temperature $t = 0$ is determined by the condition $(\partial p / \partial e) = \infty$ taken at zero polarization, where the strain polarization relations will be those for very small values of these variables and will therefore be given by Eqs. (5), which may be written

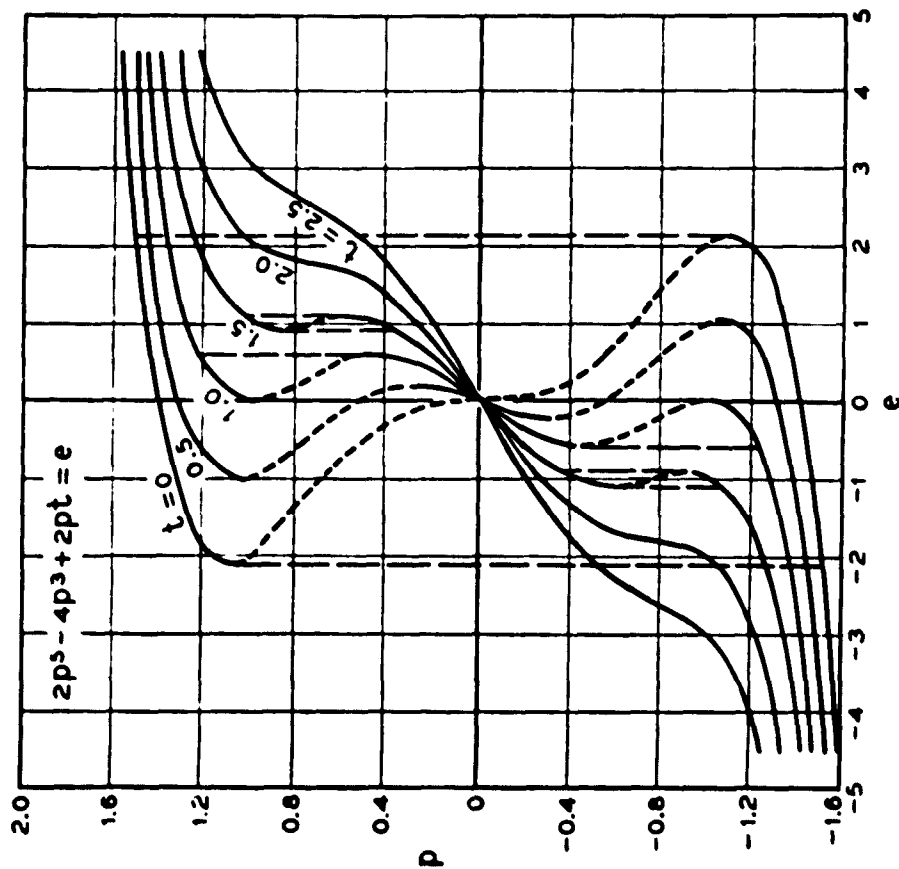


Fig. 4. Merz's isotherms of the electric field.

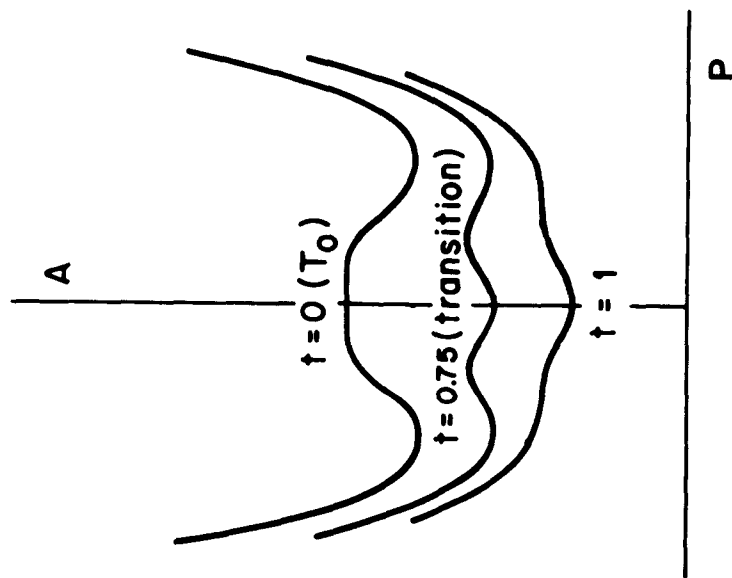


Fig. 5. Schematic representation of free energy isotherms in vicinity of transition.

$$\begin{aligned} x &= C_1 H + G_{12} P^2 \\ z &= C_2 H + G_{11} P^2 \end{aligned} \quad (5)$$

When the above strains are substituted into Eq. (14) and the Legendre transformation terms included, the terms in the free energy as a function of polarization and pressure $A_{\underline{X}, \underline{P}}$ than contain P^2 and hence determine the slope $\partial p / \partial e$ at $p = 0$, and so determine the Curie-Weiss temperature, will be

$$\begin{aligned} \frac{1}{2} \chi'' P^2 + \left\{ \left[2(c_{11} + c_{12}) C_1 G_{12} + c_{11} C_2 G_{11} + 2c_{12} (C_1 G_{11} + C_2 G_{12}) + g_{11} C_2 + 2g_{12} C_1 \right] \right. \\ \left. + \frac{2G_{12}}{2G_{12} + G_{11}} \text{ (for 2H)} \right\} H P^2 + \left[\gamma_{11} C_2^2 + 2\gamma_{14} C_1 C_2 + (2\gamma_{12} + \gamma_{13}) C_1^2 \right. \\ \left. + 3(2\delta_{11} + 2\delta_{13}) C_1^2 G_{12} + 3\delta_{11} C_2^2 G_{11} + (\delta_{12} + 2\delta_{13}) (C_1^2 G_{11} + 2C_1 C_2 G_{12}) \right. \\ \left. + 2\delta_{13} (2C_1 C_2 G_{11} + C_2^2 G_{12}) \right] H^2 P^2 \end{aligned} \quad (15)$$

Thus the linear dependence of the Curie-Weiss temperature depends entirely on the coefficients g (and, of course, c , which are known) and is given by Eqs. (13). The quadratic dependence is determined by the coefficients γ and δ , and depends, of course, also on the g and c coefficients.

For two-dimensional pressure, the linear part of the pressure shift (Eqs. 13) is seen to be proportional to the coefficient G_{12} . If one can assume that the Curie-Weiss temperature changes in more or less the same way as the transition temperature, which has yet to be checked, one would conclude that G_{12} is zero, and therefore that the x strain has no P^2 dependence at all. In Fig. 6 are plotted the strains from the X-ray data of Kay and Vousden¹⁰⁾ against the fourth power of the polarization as recently measured by Merz;⁹⁾ within 25°C of the transition temperature the x strain is directly proportional to P^4 rather than P^2 . One may object to using the results of Kay and Vousden on crystals that gave much too low value of spontaneous polarization. But Merz

10) H. F. Kay and P. Vousden, Phil. Mag. 40, 1019 (1949).

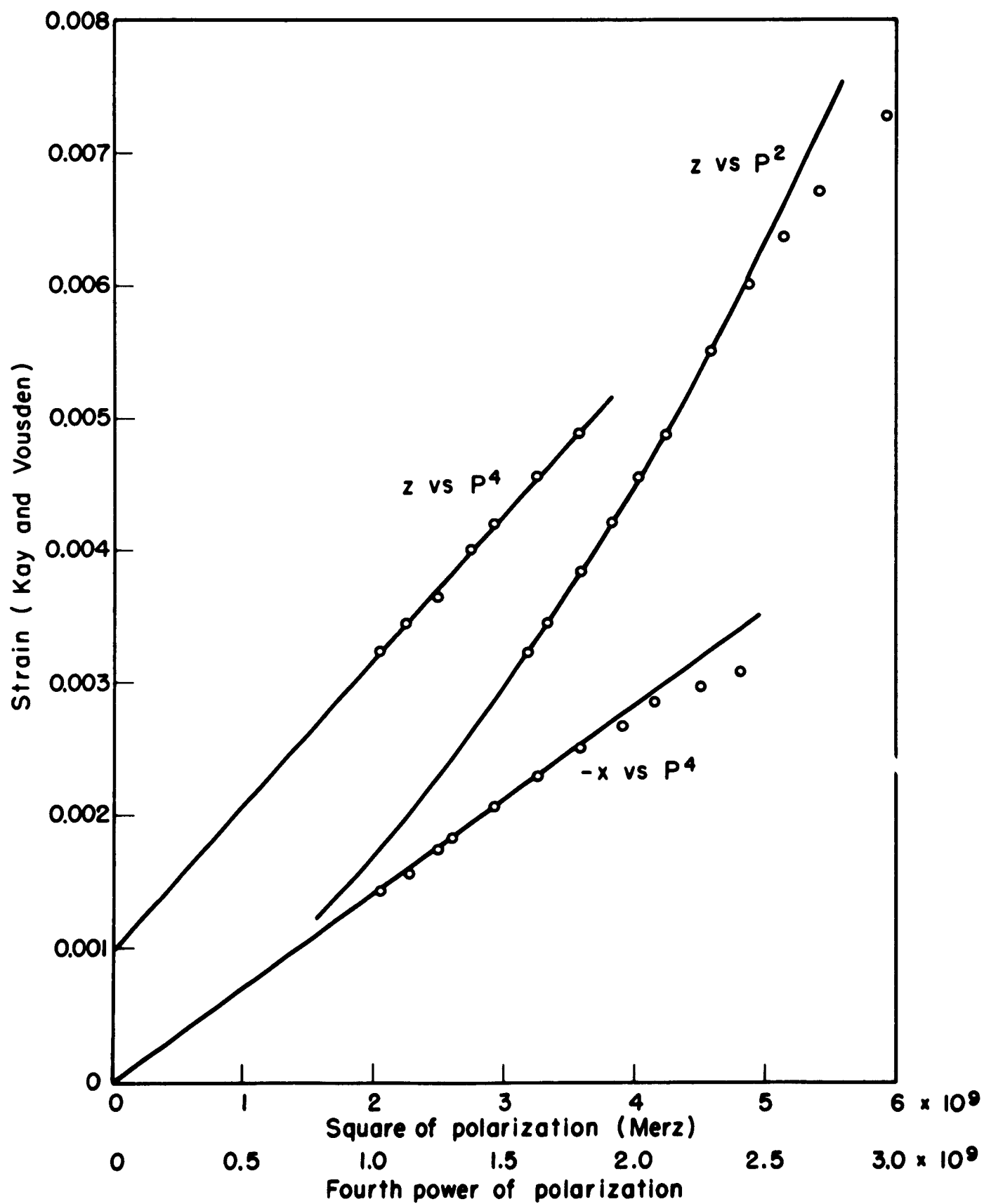


Fig. 6. Plots of the tetragonal strains against powers of the polarization.

has shown that the reason for these low values in crystals that are not exceedingly good is that some tendency to antiparallel domain formation persists to fairly appreciable fields. The X-ray parameters, however, are not affected by the existence of domains. The crystals of Merz have a somewhat lower transition temperature than those of Kay and Vousden, so the data were plotted for corresponding temperatures below the transition temperature.

The nature of the terms with coefficients γ and δ is immediately apparent upon differentiation of the free energy (Eq. 14):

$$\begin{aligned} - \frac{\partial Z}{\partial z} &= c_{11}^P + 2\gamma_{11}P^2 + 3\delta_{11}z + 2\delta_{13}(x + y) \\ - \frac{\partial X}{\partial x} &= c_{11}^P + 2\gamma_{12}P^2 + 3\delta_{11}x + 2\delta_{13}(y + z) \\ - \frac{\partial X}{\partial y} &= c_{12}^P + \gamma_{13}P^2 + \delta_{12}z + 2\delta_{13}(x + y) \\ - \frac{\partial Z}{\partial x} &= c_{12}^P + \gamma_{14}P^2 + \delta_{12}y + 2\delta_{13}(y + z) \end{aligned} \quad (16)$$

For the small polarizations and strains involved in the present discussion, one can make some qualitative statements about the γ and δ coefficients. Considering the first of the above equations, it states that the mechanical stiffness

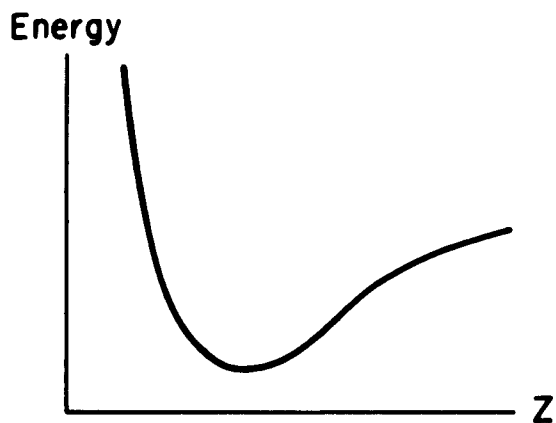


Fig. 7. Typical dependence of energy on an inter-atomic distance.

in the z direction departs from Hooke's law by the quantity $3\delta_{11}z$ when the x and y directions are clamped and the polarization is not allowed to change (since the partial derivatives are taken at constant x , y , P , in the first line). This is to be expected, since, with x , y and P clamped, the energy as a function of extension in the z direction is not a parabola, but is rather as shown in Fig. 7, which to a second approximation has a negative z^3 term in addition to the z^2

term. Hence the coefficient δ_{11} must be a negative quantity. For small changes in the clamped dimensions x and y , the shape of the energy curve in the z direction will probably not change much except to be shifted, so one would expect δ_{13} to be rather small. If one increases the fixed value of the polarization, z will be increased since $z = G_{11} P^2$, and thus γ_{11} must have the same sign as δ_{11} , i. e., negative.

Considering the second of Eqs. (16), the polarization P^2 does not change the strain x for small values, since this depends on P^4 , and therefore the coefficient γ_{12} is zero. For the same reason γ_{13} in the third equation is also zero. In the third equation, a small change in the clamped dimension z will not much affect the X, y stress-strain relation, so δ_{12} is small. In the fourth equation, where y and z are clamped, the stress Z produced by a strain x will not be influenced by P since x does not produce any P^2 , and the coefficient γ_{14} is small.

According to the foregoing, one might assume, for qualitative purposes, that $\gamma_{12} = \gamma_{13} = \gamma_{14} = \delta_{12} = \delta_{13} = 0$, for which the terms in $H^2 P^2$ in Eq. (15) reduce, since G_{12} also is zero, to $[\gamma_{11} C_2^2 + 3\delta_{11} C_2^2 G_{11}] H^2 P^2$ which is a negative quantity, since G_{11} is positive and γ_{11} and δ_{11} are both negative. This means that the Curie-Weiss temperature will rise quadratically with two-dimensional pressure. Using Mason's¹¹⁾ values $c_{11}^P = 2.07 \times 10^{12}$ and $c_{12}^P = 1.40 \times 10^{12}$ the value of C_2^2 for two-dimensional pressure is about 18 times that for hydrostatic pressure, so that the quadratic effect for hydrostatic pressure is 18 times smaller.

Finally, we may consider the linear dependence of the Curie-Weiss temperature on hydrostatic pressure. If the linear effect for two-dimensional pressure is absent, then $c_{11}g_{12} - c_{12}g_{11} = 0$ from which $g_{12} = 0.68 g_{11}$. In order to match the dependence of the Curie-Weiss temperature on hydrostatic pressure to

11) W. L. Bond, W. P. Mason, and H. J. McSkimin, Phys. Rev. 82, 442 (1951).

Mézi's³⁾ measurement of the transition, it is necessary to assume $g_{11} = -0.33$. Assuming $z = aP^2 + bP^4$ one can match the z strain in Fig. 6 quite accurately within 25°C of the transition by assuming $a = 0.57 \times 10^{-12}$, which requires a value for g_{11} of -1.2 . The curve in Fig. 6 suggests a negative P^6 term in the strains; this could reduce the coefficient a and thus g_{11} .

Probable Effect on the Hysteresis Loop

If the shift remains quadratic to much higher pressures, a two-dimensional pressure of 2000 atm. should raise the transition by more than 100°C . This should result in a marked increase of the coercive field at room temperature. One would then have a hysteretic circuit element with a variable switching field. The pressure could easily be controlled by a screw, driven by a small hand wheel. For one operating temperature, room temperature, the clearance between the crystal and the clamp could be made sufficiently small to prevent extrusion of the rubber at quite high pressures.

It is possible that at room temperature the hysteresis loop is affected by the proximity of the orthorhombic transition around 5°C , since the direction of the polarization might well reverse by a rotation through the orthorhombic configurations rather than by direct passage through the cubic configuration. In this case, the effect of the two-dimensional pressure on the orthorhombic transition would enter into the picture. It is expected that the two-dimensional pressure, as presently applied to two of the pseudo-cubic axes, will cause a very large depression of the orthorhombic transition. The reason for expecting this is that the elongation that accompanied the spontaneous polarization would be working in part against a component of compression, when the polarization direction snaps into a new direction at 45° to the direction in which there is no component of stress. The rhombohedral phase would likewise be suppressed by the two-dimensional pressure as applied at present. Thus a

high enough pressure would result in a behavior much more like that of lead titanate: a Curie point around 500°C , probably no lower phase transitions, a high coercivity, and possibly even an order-disorder type of transition, as mentioned in the introduction. From the magnitudes of the effects of two-dimensional and of hydrostatic³⁾ pressures on the orthorhombic transition, it will be possible to obtain information about the shear terms in Devonshire's expansion.

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